Supporting information for

From Polyamines to Nanogels: A Supramolecular Approach for Boosting Relaxivity of [Gd(DOTP)]$^{5-}$

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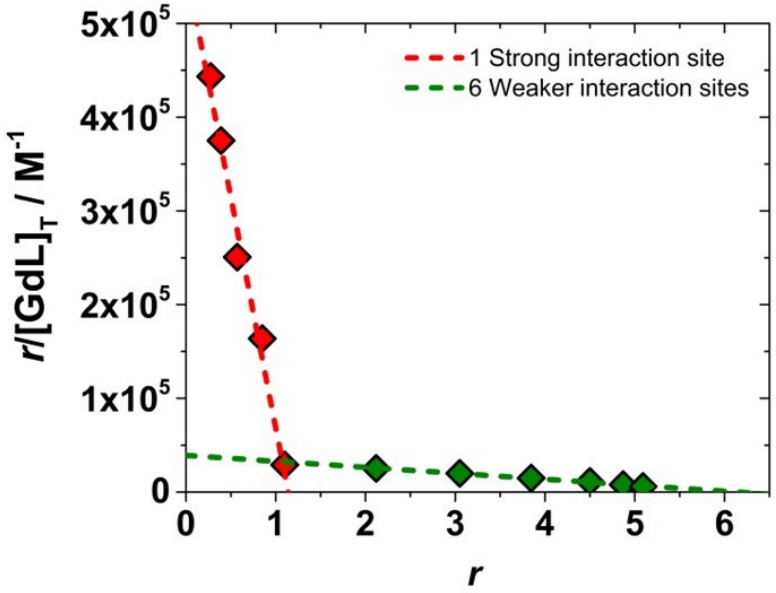

Figure S1. Scatchard plot of the reverse titration investigating the $[Gd(HDOTP)]^{4-}$ and PEI interaction.

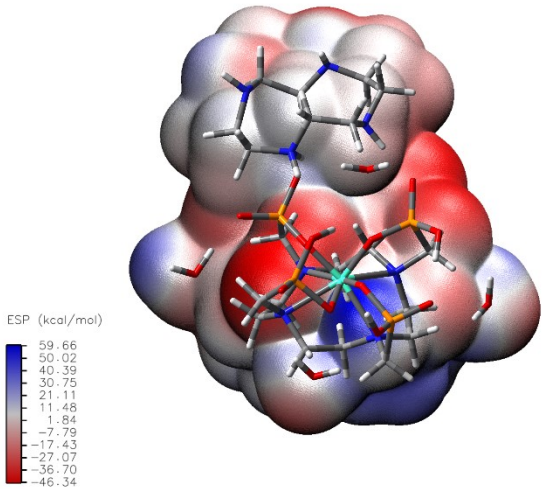

Figure S2. Molecular electrostatic potential ESP (PBE0 aug-pcseg1 D3) of the supramolecular complex A) $[Gd(DOTP)]^{5-}$ and 1 Cyclen unit, plotted on the 0.001 au contour of the electron density. Color code: grey = C, white = H, red = O, blue = N, orange = P, light blue = Gd.

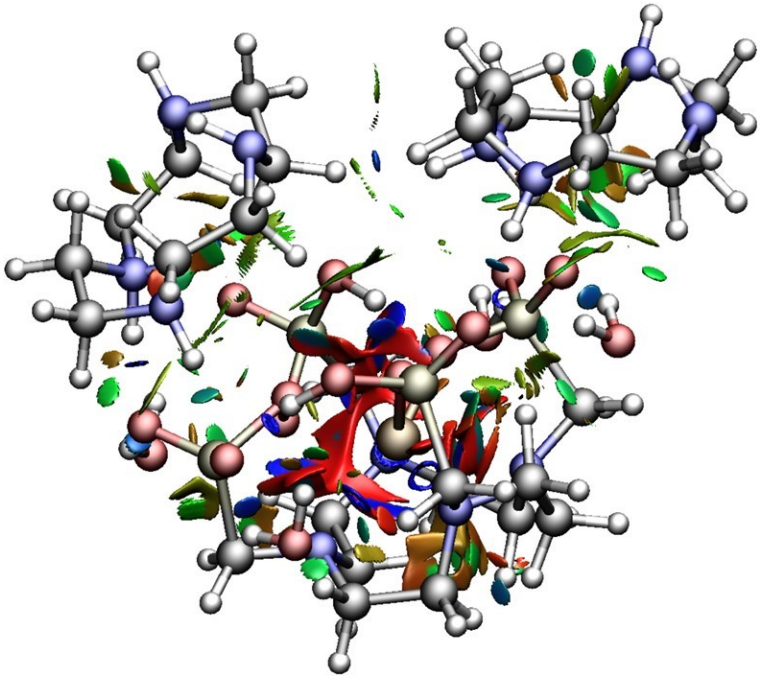

Figure S3. Isosurface maps of NCI=0.4 for the complex $[Gd(DOTP)]^{5-}$/Cyclen (1:2). Blue regions are associated with strong hydrogen bonds or coordination bonds, green regions with dispersive interactions and tan-to-red regions with repulsive interactions. Atoms color: H = white, C = grey, N = violet, O = red, P = tan, Gd = metallic grey.

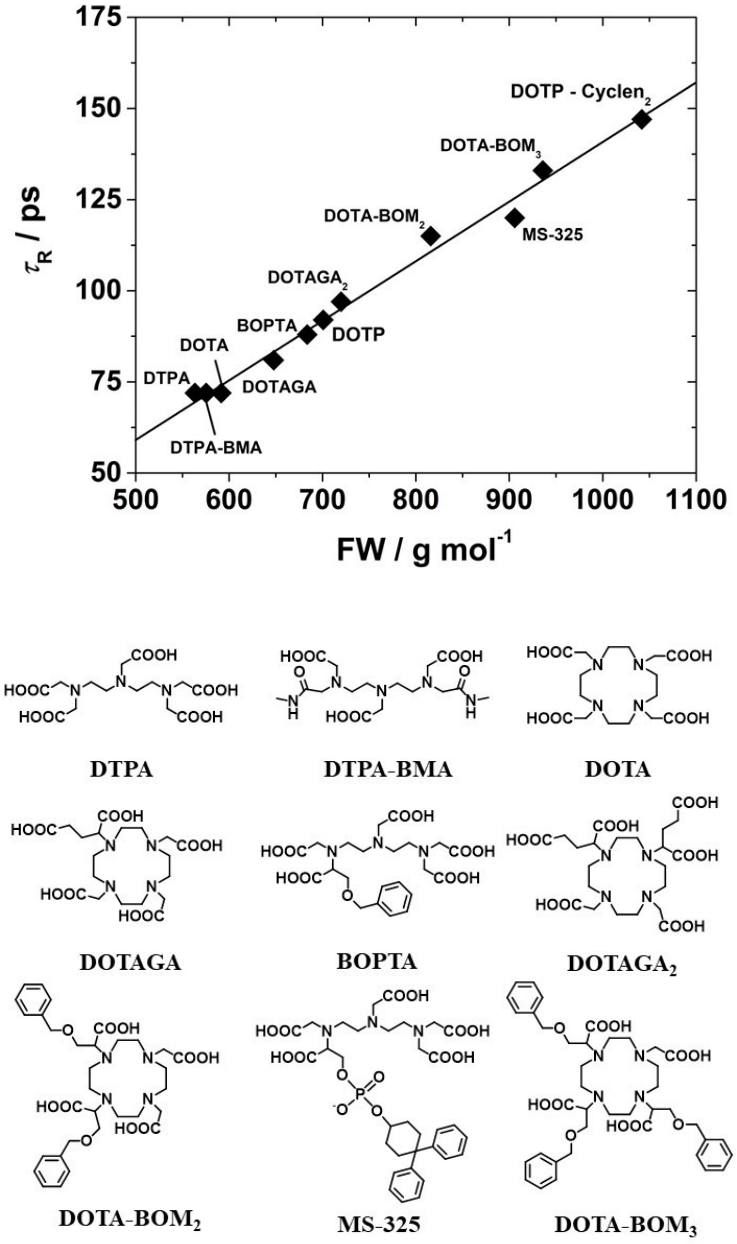

Figure S4. Reorientational correlation time (τ_R) versus molecular mass for Gd(III)-complexes with ligands DTPA[(1)], DOTA[(1)], DTPA-BMA[(1)], DOTAGA[(2)], BOPTA[(3)], DOTP[(4)], DOTAGA$_2$[(2)], DOTA-BOM$_2$[(5)], DOTA-BOM$_3$[(5)] and MS-325[(6)].

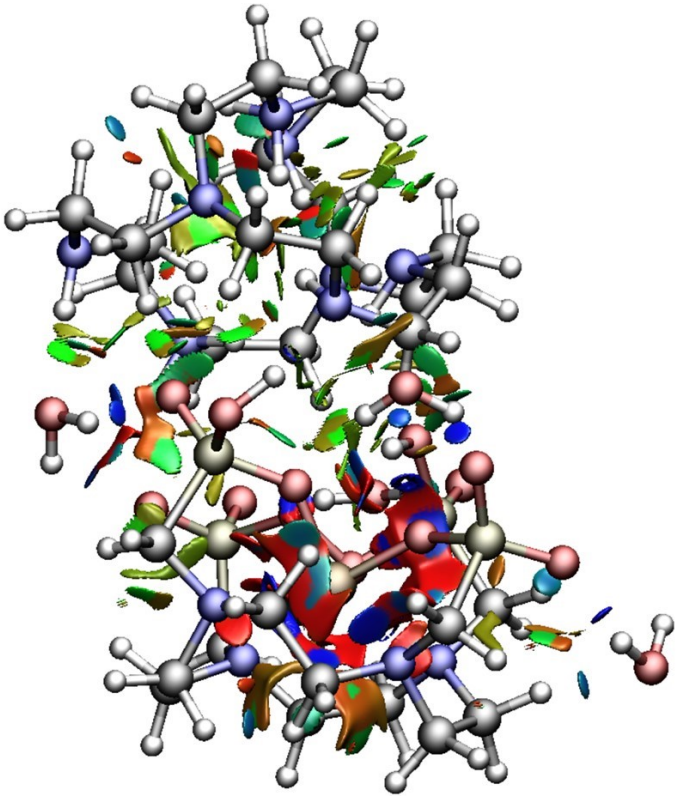

Figure S5. Isosurface maps of NCI=0.4 for the complex $[Gd(HDOTP)]^{4-}$/octaazacryptand. Blue regions are associated with strong hydrogen bonds or coordination bonds, green regions with dispersive interactions and tan-to-red regions with repulsive interactions. Atoms color: H = white, C = grey, N = violet, O = red, P = tan, Gd = metallic grey.

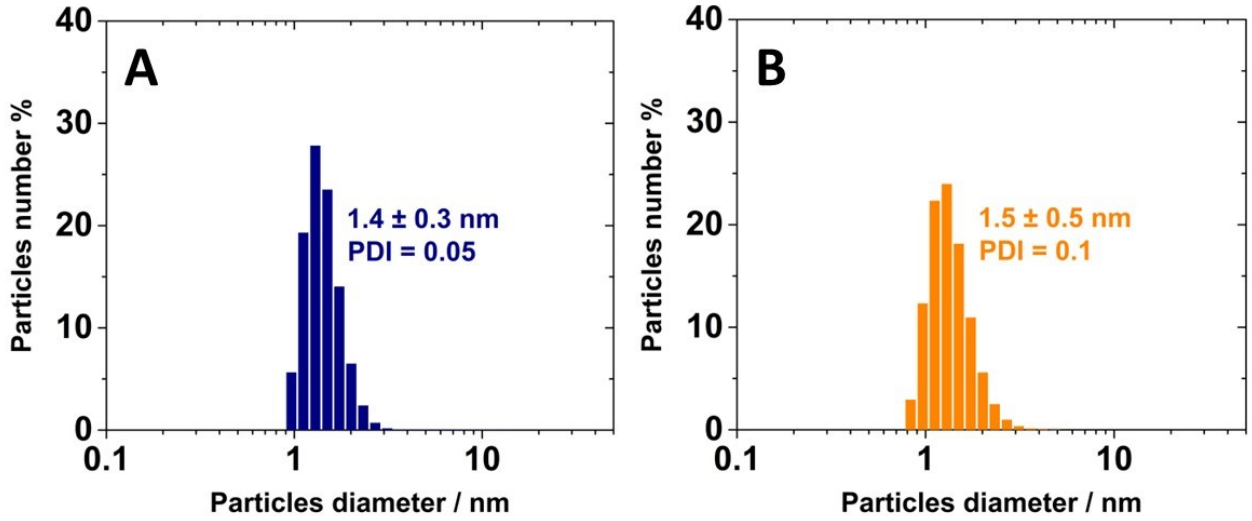

Figure S6. DLS analysis for $[Gd(HDOTP)]^{4-}$ (1 mM) in the presence of octaazacryptand (A, 50 mM) and PEI (B, 1 mM).

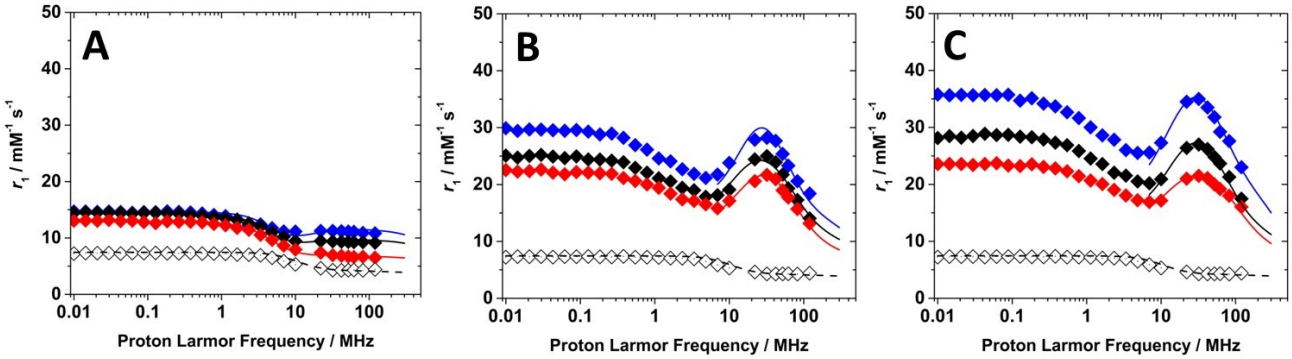

Figure S7. ^{1}H NMRD profiles for the adducts with (A) cyclen (pH 9.0), (B) octaazacryptand (pH 7.1) and (C) PEI (pH 7.2), at different temperatures (♦ = 283 K, ♦ = 298 K, ♦ = 310 K). The ^{1}H NMRD of $[Gd(DOTP)]^{5-}$ (◊, pH 7.5 and 298 K) is reported for comparison.

Table S1. Parameters (298 K) obtained by the analysis of ^{1}H NMRD profiles of the $[Gd(DOTP)]^{5-}$ and the different adducts.

	$[Gd(DOTP)]^{5-}$	-2	-3	-4	NG/$[Gd(DOTP)]^{5-}$
Δ^2 / 10^{20} s^{-2}	9.0 ± 0.2	4.1 ± 0.3	/	/	/
τ_V / ps	17 ± 1	22 ± 2	/	/	/
τ_{RL}^{SS} / ps	/	/	135 ± 10	202 ± 15	610 ± 34
τ_{RG}^{SS} /ns	0.040 ± 0.002	0.150 ± 0.003	3.5 ± 0.6	6.0 ± 0.8	10.0 ± 0.9
S^2	/	/	0.16 ± 0.01	0.22 ± 0.01	0.30 ± 0.02
τ_M^{SS} / ns	1.0 ± 0.1	1.0 ± 0.2	6.0 ± 0.9	1.9 ± 0.2	2.9 ± 1.7
ΔH_M^{SS} / kJ mol^{-1}	15.0 ± 0.2	13.7 ± 0.1	12.0 ± 0.4	10.0 ± 0.3	13.5 ± 0.3
q^{SS}	4*	3.9 ± 0.1	4.0 ± 0.1	4.1 ± 0.2	3.1 ± 0.3
r_{Gd-H}^{SS} / Å	3.5*	3.5*	3.5*	3.5*	3.5*
a_{Gd-H} / Å	4.0*	4.0*	4.0*	4.0*	4.0*

*fixed during the analysis

Computed Coordinates

[Gd(HDOTP)]$^{4-}$/octaazacryptand:

Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
Gd							-2.4374852	0.0415717	0.3775961
P	1			2.8201805			-1.7701736	0.8898119	-2.2278984
N	1	2		2.4193429	62.7237194		-4.2278268	0.1489024	-1.2460963
O	2	1	3	1.7721012	50.2191339	92.9080467	-2.2186956	1.8452446	-0.8044100
C	3	1	4	1.4894376	104.7766305	56.3981888	-3.5403933	0.2571112	-2.5629678
H	5	3	1	1.1193237	115.3684420	-142.1002177	-4.0331267	0.9326883	-3.3070747
H	5	3	1	1.1467487	110.1662079	98.9121855	-3.4953748	-0.7699739	-3.0710052
C	3	1	4	1.5057054	124.2099119	-175.6784849	-5.3592796	-0.8413914	-1.3253542
H	8	3	1	1.1400726	110.0204021	-103.3484860	-5.1882982	-1.5607423	-2.1931475
H	8	3	1	1.1163184	113.2701950	140.5909463	-6.3442423	-0.3683005	-1.5538280
O	2	1	4	1.4993240	156.5271373	13.9743160	-1.3826378	1.8633733	-3.3002634
C	3	1	4	1.5157324	90.7721008	-59.0164476	-4.6938762	1.4733652	-0.6750965
H	12	3	1	1.1267955	111.2776262	-160.0384827	-5.7621217	1.6889191	-0.9615511
H	12	3	1	1.1386644	112.5353576	84.7730610	-4.1257787	2.3597152	-1.1089231
C	8	3	1	1.5511169	110.8993882	17.0713761	-5.4714538	-1.6596236	-0.0123893
N	15	8	3	1.5161008	110.0797720	-37.9787320	-4.0890444	-1.9702814	0.5270523
C	16	15	8	1.4874995	109.3468760	-94.5999145	-3.6646718	-3.3140155	0.0506685
P	17	16	15	1.9375257	100.3109892	103.6275949	-2.4167502	-2.8097107	-1.3430224
O	18	17	16	1.6603362	101.1232676	21.1797858	-2.0343228	-1.2602324	-0.8852205
O	18	17	16	1.5240810	108.6544853	-93.4225294	-3.1620076	-2.7645111	-2.6716951
H	17	16	15	1.1080903	115.5997953	-14.3681125	-4.4683514	-3.9467701	-0.3754589
H	17	16	15	1.1083458	115.5153218	-139.0832698	-3.1424701	-3.9429422	0.7991248
C	16	15	8	1.5131622	111.1630273	142.7926348	-4.0650169	-1.9046693	2.0386004
H	23	16	15	1.1240632	111.8420891	83.2300445	-4.4224348	-2.8631422	2.5045406
H	23	16	15	1.1320934	109.9327958	-33.1618831	-4.7871219	-1.1121344	2.4020400
C	23	16	15	1.5534045	109.8582094	-156.0360026	-2.6193746	-1.6215464	2.5315761
N	26	23	16	1.5234817	115.1325452	95.0839439	-2.3020741	-0.1554859	2.7980034
C	27	26	23	1.4960416	111.2198187	169.0092965	-0.9960999	-0.0052228	3.5121414
P	28	27	26	1.8924362	102.5149538	76.3110458	0.2630850	-0.2957897	2.1296295
O	29	28	27	1.5768135	105.0273250	4.7050111	-0.5979124	-0.4442012	0.8169992
O	29	28	27	1.6670923	101.1824793	-107.3721880	0.8428629	-1.8059946	2.5325382
H	28	27	26	1.1122260	115.6439032	-46.2201289	-0.8388578	-0.6873166	4.3764732
H	28	27	26	1.1271982	110.6859463	-168.8579895	-0.8646111	1.0508536	3.8836101
C	27	26	23	1.5070664	114.0469570	45.6182272	-3.3668021	0.5712394	3.5786914
H	34	27	26	1.1207575	112.7126400	97.1824801	-3.1371005	0.6283498	4.6741698
H	34	27	26	1.1212176	112.1741568	-20.1191530	-4.3574376	0.0482356	3.5313912
C	34	27	26	1.5516642	108.7485409	-142.4567155	-3.4922448	2.0156286	3.0258209
N	37	34	27	1.5169112	111.8486116	38.9290118	-3.3618050	2.0551299	1.5150448
C	38	37	34	1.4908685	109.3133708	-162.1211823	-3.0550716	3.4486276	1.0828787
P	39	38	37	1.9097104	94.0201564	98.2149764	-1.1775714	3.1325271	0.9343290
O	4	2	1	1.4466067	100.2543508	67.7906749	-1.0676259	1.6070063	0.0387697
O	40	39	38	1.5236483	110.4858778	-65.7133597	-0.5764419	2.8381768	2.3030896
H	39	38	37	1.1078946	117.1325848	-19.0690513	-3.2840130	4.2618569	1.7995896
H	39	38	37	1.1116056	115.6041685	-144.8355786	-3.5055309	3.7619114	0.1161281

C	38	37	34	1.5199384	109.2735355	71.3845007	-4.6075087	1.4508181	0.8879545
H	45	38	37	1.1271853	110.5788235	53.9186260	-5.5344132	1.9592716	1.2789400
H	45	38	37	1.1704907	105.4737679	-62.0481957	-4.6337985	0.3394382	1.2542772
H	37	34	27	1.1169744	109.5758100	164.9120404	-4.4419370	2.4754535	3.3922598
H	37	34	27	1.1279551	107.9480792	-80.4661920	-2.6617248	2.6329506	3.4746336
H	26	23	16	1.1259857	108.3321525	-140.3905539	-2.4307210	-2.2431329	3.4512956
H	26	23	16	1.1830222	107.4728612	-24.5126636	-1.8772641	-1.9968024	1.6901507
H	15	8	3	1.1158064	110.1625317	85.8957674	-6.0946748	-1.1092429	0.7317213
H	15	8	3	1.1213693	107.8861295	-160.4608940	-6.0542484	-2.5912209	-0.2358757
O	40	39	38	1.5088695	113.0957167	159.6810695	-0.4754664	4.1393044	0.0567557
O	29	28	27	1.5212322	116.0058216	138.2448143	1.4682028	0.6325034	2.1191225
O	18	17	16	1.5238350	106.8862130	135.7664488	-1.1931466	-3.7043383	-1.1864692
O	2	1	19	1.6191343	81.3795786	-59.9302353	-0.3955171	0.1148729	-1.8654279
H	57	2	1	1.1337781	118.4442130	22.2242634	-0.4196302	-0.6767117	-1.0540925
O	42	40	39	2.4405563	131.9243336	-154.9518334	1.6852972	3.1012255	3.1815297
H	59	42	40	0.9998458	38.3934890	94.3968450	0.8062609	3.5744013	3.1259278
H	59	42	40	1.0011681	68.9516338	-117.9486507	1.4043893	2.1403485	3.1935209
O	54	40	39	2.8995734	134.7443780	-76.9429168	-0.2538024	4.5491962	-2.8051282
H	62	54	40	0.9760963	15.0646565	96.2206672	-0.5145847	4.5852212	-1.8652034
H	62	54	40	0.9730233	102.8830556	-6.2299211	-0.6999999	3.7660379	-3.1716595
O	20	18	17	2.4084229	151.1856749	17.4305868	-5.2050200	-2.6599299	-3.9427828
H	65	20	18	0.9679682	60.5113504	153.3032872	-4.3862823	-2.3155979	-4.3275769
H	65	20	18	0.9845109	46.3537892	-57.5464080	-4.8579723	-3.2832718	-3.2643548
O	56	18	17	2.4295968	163.0648147	-2.2642120	0.3810984	-5.3684478	-0.3768813
H	68	56	18	0.9765748	55.0454600	112.1249715	-0.1107598	-5.4263437	-1.2185593
H	68	56	18	0.9840435	47.9003122	-49.4517865	-0.1061963	-4.6447829	0.0783050
N	57	2	1	3.9698059	116.0453348	-126.5537912	2.9523842	2.1991904	-2.3198910
C	71	57	2	1.5035431	52.3370433	-88.3956827	2.2429556	1.3644198	-3.3497020
H	72	71	57	1.1104991	113.0562477	136.2040096	2.1768393	1.8603309	-4.3411198
H	72	71	57	1.1257786	109.2248867	20.4135867	1.1713374	1.2206155	-3.0361225
C	72	71	57	1.5406188	110.9725956	-99.5430484	2.9083577	-0.0177031	-3.4928196
H	75	72	71	1.1135643	108.0094249	-174.7537372	2.4079489	-0.5557392	-4.3295594
H	75	72	71	1.1096571	110.6934406	-58.6949684	3.9742280	0.0883733	-3.7826594
N	75	72	71	1.5031181	112.7094657	61.0893963	2.8770065	-0.8117496	-2.2169390
C	78	75	72	1.5014984	112.7984310	120.7844728	2.1578472	-2.1215524	-2.3643294
H	79	78	75	1.1087271	107.4005386	92.7406603	2.9163351	-2.8896202	-2.6173980
H	79	78	75	1.1167795	112.8322571	-23.9632584	1.4229288	-2.1201865	-3.2052156
C	79	78	75	1.5347410	111.7592059	-145.2487568	1.3963258	-2.4994247	-1.0865472
H	82	79	78	1.1301749	110.4100457	67.1812172	0.5423611	-1.7806055	-0.9095205
H	82	79	78	1.1331884	109.6228013	-179.9255997	0.8695631	-3.4914294	-1.2367601
N	82	79	78	1.4840593	116.3540638	-54.4251024	2.1891518	-2.5321399	0.1675615
C	85	82	79	1.4932269	112.7186448	-76.4145157	3.0454697	-3.7505402	0.2768631
H	86	85	82	1.1073796	113.4530591	58.6154218	3.7656133	-3.8593882	-0.5573040
H	86	85	82	1.1281218	107.4286453	-58.0756341	2.3649755	-4.6483033	0.2167979
C	86	85	82	1.5393240	109.0740833	-176.6668547	3.7632943	-3.7403865	1.6385324
H	89	86	85	1.1177170	108.0052501	64.2783755	2.9870032	-3.8181986	2.4389128
H	89	86	85	1.1090296	109.7037065	178.8878596	4.3872709	-4.6516977	1.7390895
N	89	86	85	1.5068342	110.0637895	-56.4891405	4.5580776	-2.4697354	1.7944640

C	71	57	2	1.4961657	75.1362136	41.1378789	1.9819723	3.1601444	-1.7088429
H	93	71	57	1.1223704	108.3110273	-2.0244482	0.9962127	2.6371654	-1.5884836
H	93	71	57	1.1254242	113.3708866	-115.4448343	1.7253603	4.0244221	-2.3824556
C	93	71	57	1.5309868	114.4374024	119.5986520	2.4144291	3.7194961	-0.3508931
H	96	93	71	1.1060912	111.7576870	64.0057288	3.3352541	4.3268904	-0.4320794
H	96	93	71	1.1366036	105.9449930	-179.7096646	1.5812169	4.4189272	-0.0216190
N	96	93	71	1.5178336	113.6779123	-62.1652485	2.5646031	2.6595506	0.7251097
C	99	96	93	1.5178490	113.1134315	111.3251827	4.0054127	2.4417259	1.1499460
H	100	99	96	1.1204041	107.9657670	95.8350529	4.1931736	3.0603155	2.0650406
H	100	99	96	1.1170843	110.3947386	-20.4240901	4.7041678	2.8144488	0.3621034
C	100	99	96	1.5403087	111.6928944	-143.0200770	4.2933675	0.9579680	1.4467546
H	103	100	99	1.1176072	110.4692294	20.5217215	3.5331684	0.3055845	0.9512358
H	103	100	99	1.1150859	108.8261065	138.8215868	5.2940569	0.6953986	1.0307081
N	103	100	99	1.4913434	108.0990871	-102.5529837	4.3114992	0.7766161	2.9269194
C	106	103	100	1.4816922	113.8938266	-163.2936310	4.9509396	-0.4846880	3.3692312
H	107	106	103	1.1185443	105.4373586	169.2180476	5.0693975	-0.3858956	4.4770891
H	107	106	103	1.1143457	109.0901820	56.4590102	5.9879555	-0.5292660	2.9637968
C	92	89	86	1.5014219	109.7937597	127.1011350	4.1911925	-1.7956744	3.0849309
H	110	92	89	1.1114676	111.8378315	54.6334264	4.3094169	-2.4767199	3.9553102
H	110	92	89	1.1279614	105.5662773	-60.1410245	3.0870446	-1.5778426	3.0094083
C	71	57	2	1.4988298	163.8540739	-83.2905061	4.1695153	2.8617708	-2.8909164
H	113	71	57	1.1118110	112.3919220	106.5346135	4.0505355	3.9638021	-2.9774870
H	113	71	57	1.1103377	111.1403262	-11.4296472	4.3738489	2.5037537	-3.9218972
C	113	71	57	1.5508357	109.5476265	-132.2905596	5.3957033	2.5585732	-1.9911244
H	116	113	71	1.1070177	109.9577666	168.6208806	6.3267689	2.8657661	-2.5051649
H	116	113	71	1.1230286	109.1238477	-74.7776328	5.3270053	3.1757603	-1.0554139
N	116	113	71	1.4928126	114.2993860	41.7295596	5.4663821	1.1494182	-1.5035013
C	119	116	113	1.4923609	114.5568303	95.9942171	6.3323114	0.2521119	-2.3233481
H	120	119	116	1.1142125	107.3170948	74.9338825	7.3910817	0.5071016	-2.0878584
H	120	119	116	1.1147598	114.0161956	-42.6337249	6.2130482	0.3875376	-3.4234052
C	120	119	116	1.5434031	110.3407140	-164.5771550	6.0438303	-1.2262234	-1.9866040
H	123	120	119	1.1245304	109.4294665	85.6749258	5.1774776	-1.5886098	-2.6052136
H	123	120	119	1.1106412	109.6503832	-157.4226866	6.9201567	-1.8500976	-2.2629318
N	123	120	119	1.5235260	112.3044831	-33.6045893	5.6748663	-1.4242228	-0.5217514
C	126	123	120	1.5191337	113.2284764	-137.2946469	6.3378891	-2.6392991	0.1041540
H	127	126	123	1.1117205	110.2758631	53.1129744	7.4376737	-2.6023460	-0.0540579
H	127	126	123	1.1164157	109.0241094	-64.4847798	5.9600614	-3.5605386	-0.4007698
C	92	89	86	1.4905710	112.0840982	-104.7786250	6.0203148	-2.6979789	1.6167871
H	130	92	89	1.1133360	114.2803721	-36.1256423	6.3837596	-3.6711216	2.0173094
H	130	92	89	1.1182892	109.9059466	-155.0552045	6.5975617	-1.9081142	2.1585161
H	78	75	72	1.0383900	107.0448588	2.0333825	2.3665151	-0.2409249	-1.5156463
H	99	96	93	1.0483431	110.6801382	-12.5580291	2.1429541	1.7521350	0.4123283
H	99	96	93	1.1253369	111.0702740	-128.2857760	1.9864993	2.9370608	1.6498622
H	119	116	113	1.0438942	106.4771601	-25.4923521	4.4871472	0.7877501	-1.5002998
H	85	82	79	1.0294586	110.2860833	46.2535972	2.7785796	-1.6911748	0.2392387
H	31	29	28	1.0452006	114.8778187	151.1696322	1.1763298	-2.3789384	1.7244667
H	106	103	100	1.0390153	108.2625134	73.3235074	3.3335000	0.8305440	3.2735635
H	126	123	120	1.0611636	108.8936540	101.3127334	4.6216143	-1.5272718	-0.4435897

H	126	123	120	1.0584301	110.7710671	-13.6617808	5.9082167	-0.5607409	0.0441292

$[Gd(DOTP)]^{5-}$/Cyclen (1:2)

Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
Gd							-0.7194981	-1.6528088	0.2872012
P	1			2.8605851			-0.9846062	-0.4670105	-2.3024990
N	1	2		2.4469315	61.2867400		-0.8591881	-3.1177099	-1.6677989
O	2	1	3	1.7573726	49.6325072	90.5908531	-2.2119029	-0.9604190	-1.1454989
C	3	1	4	1.4897014	106.3152934	56.0281812	-0.6271940	-2.2514082	-2.8572990
H	5	3	1	1.1223142	115.0782072	-140.4103615	-1.2716925	-2.4820127	-3.7466991
H	5	3	1	1.1403364	111.3132420	101.4597142	0.4378068	-2.3624010	-3.2494990
C	3	1	4	1.5072654	125.7800534	-173.7499452	-0.1337791	-4.4275050	-1.8411989
H	8	3	1	1.1304438	110.6199477	-108.6961525	0.6889203	-4.3281994	-2.6100990
H	8	3	1	1.1168943	113.2466955	135.0240062	-0.7836736	-5.2413095	-2.2446990
O	2	1	4	1.5053146	156.4610278	14.8600201	-1.6871110	0.2359847	-3.4330990
C	3	1	4	1.5193615	87.8548322	-59.4335081	-2.3191866	-3.3507199	-1.3176989
H	12	3	1	1.1276100	111.1446764	-159.6574490	-2.7065802	-4.2952226	-1.7965989
H	12	3	1	1.1536501	113.3595983	87.0160308	-3.0292920	-2.5610247	-1.7682989
C	8	3	1	1.5489543	110.0836747	11.9582792	0.4836240	-4.8761008	-0.4932988
N	15	8	3	1.5154234	109.5459348	-37.1510422	0.9933158	-3.6635973	0.2594012
C	16	15	8	1.4931640	108.7167571	-90.5992677	2.4196143	-3.4310875	-0.1162988
P	17	16	15	1.9048243	101.5148166	117.9750583	2.3254025	-1.7053880	-0.9171989
O	18	17	16	1.6343663	104.7781428	4.4134530	0.7730992	-1.2358986	-0.7144988
O	18	17	16	1.5336690	112.8373034	-114.5759261	2.6618026	-1.7243858	-2.4133990
H	17	16	15	1.1118972	114.9810249	-1.0978726	2.8421193	-4.1674847	-0.8342989
H	17	16	15	1.1158000	115.0639297	-124.1424361	3.1351141	-3.4019826	0.7394013
C	16	15	8	1.5114691	110.6748009	147.3105662	0.8532171	-3.8636982	1.7510013
H	23	16	15	1.1259612	111.6496390	85.7816771	1.7385209	-4.4099922	2.1818014
H	23	16	15	1.1299037	110.4558184	-30.1747398	-0.0308784	-4.5294043	1.9788014
C	23	16	15	1.5470299	110.2261206	-153.8678160	0.7332078	-2.4965990	2.4651014
N	26	23	16	1.5220315	116.3149688	92.7743576	-0.6789958	-1.9802086	2.7009014
C	27	26	23	1.4925890	109.6113459	164.2041512	-0.6485033	-0.8812083	3.7104015
P	28	27	26	1.9027996	101.1134547	81.7946814	-0.1502134	0.6000952	2.6250014
O	29	28	27	1.6023492	101.8420009	7.6050887	-0.2167091	-0.0327053	1.1544013
O	29	28	27	1.4985535	114.0313055	-118.9916188	1.1440823	1.2412041	3.0243014
H	28	27	26	1.1134380	115.6561730	-38.8829552	0.0593977	-1.0245035	4.5578015
H	28	27	26	1.1245541	112.7918412	-160.8616748	-1.6531047	-0.6922151	4.1791015
C	27	26	23	1.5030177	116.0558450	39.6286726	-1.6976889	-3.0069156	3.1098014
H	34	27	26	1.1233861	112.7530957	95.0306680	-1.8282885	-3.0697165	4.2238015
H	34	27	26	1.1228424	112.2084764	-22.6704661	-1.4008818	-4.0452136	2.8022014
C	34	27	26	1.5520062	107.8363546	-145.5396430	-3.0586918	-2.6019249	2.4834014
N	37	34	27	1.5183653	113.1882440	48.3901390	-2.9601941	-2.2644242	1.0063013
C	38	37	34	1.4914207	109.0829219	-173.0453235	-4.2716978	-1.7288331	0.5400012
P	39	38	37	1.8898194	95.7327835	107.3170447	-3.6974100	0.0645710	0.3809012
O	4	2	1	1.4504228	100.5376075	70.4518612	-2.0228097	0.0420824	-0.1144988
O	40	39	38	1.5262603	113.5558106	-80.8350702	-3.6782152	0.8188712	1.7076013
H	39	38	37	1.1108402	116.7284346	-11.2810770	-5.1312971	-1.8372389	1.2352013

H	39	38	37	1.1178090	115.6119492	-135.5682149	-4.6371951	-2.1293356	-0.4374988
C	38	37	34	1.5258975	109.3858322	61.9015952	-2.4884856	-3.4943210	0.2361012
H	45	38	37	1.1281516	110.0472947	57.2362790	-3.1927798	-4.3570259	0.4162012
H	45	38	37	1.1785642	106.1924013	-58.5105319	-1.4461835	-3.7920139	0.6987013
H	37	34	27	1.1190041	109.0564970	174.3905712	-3.8092863	-3.4059300	2.6892014
H	37	34	27	1.1324937	107.8109297	-71.2655686	-3.4331981	-1.6846273	3.0319014
H	26	23	16	1.1300621	107.9059560	-141.9332574	1.3062083	-2.5607951	3.4370015
H	26	23	16	1.1839147	108.9699338	-28.4741081	1.3033022	-1.6779950	1.8275013
H	15	8	3	1.1165291	110.1747592	86.0668777	-0.2681722	-5.4460060	0.1039012
H	15	8	3	1.1204101	108.4259089	-160.0122458	1.2965291	-5.6173954	-0.7053988
O	40	39	38	1.5329586	109.0036715	145.4377879	-4.4168145	0.7156661	-0.8058988
O	29	28	27	1.6530505	105.5357480	121.6233242	-1.3680210	1.7045870	2.7971014
H	55	29	28	1.0507198	116.2861823	-72.5422575	-2.2766195	1.4730808	2.3229014
O	18	17	16	1.5535546	106.1725692	121.5201212	3.2831964	-0.7958814	-0.0992988
O	2	1	19	1.6306062	81.9691342	-59.2258159	-0.1081142	0.7146955	-1.5994989
H	57	18	17	1.5356730	120.7671484	176.4982813	3.5248864	0.6632203	-0.5126988
H	58	2	1	1.1272206	115.8427174	1.7273089	0.1997871	0.5287976	-0.5311988
H	54	40	39	1.6437018	121.0904968	-150.9790193	-3.7158228	1.9330710	-1.6592989
O	42	40	39	2.6497234	137.9019887	20.9030621	-3.5954113	0.2467717	4.2935015
H	62	42	40	0.9778948	30.2136191	-80.1971134	-4.1051119	0.3366682	3.4638015
H	62	42	40	0.9628362	82.6976632	143.4743669	-3.0433166	1.0349755	4.3248015
O	4	2	1	2.7857625	98.9780018	-158.8928560	-4.3761014	-1.2001337	-2.8830990
H	65	4	2	0.9833871	79.5689228	-117.5427245	-4.7003063	-0.4836359	-2.2926990
H	65	4	2	0.9645030	85.2969051	-11.4396803	-3.8089044	-0.7555298	-3.5240990
O	20	18	17	2.6159871	124.3257069	38.3563848	1.9395155	-3.6211908	-4.0637991
H	68	20	18	0.9419247	109.6292759	-178.8986361	2.2694143	-3.4331886	-4.9257991
H	68	20	18	1.0182145	11.4017495	-106.8909061	2.4048111	-2.9644876	-3.4400990
O	57	18	17	2.8531075	121.8129280	-45.8698704	3.2889964	-0.7986814	2.7538014
H	71	57	18	0.9841193	16.7952639	166.2656390	3.5336954	-0.6561797	1.8113013
H	71	57	18	0.9708075	107.0010552	-107.5587884	2.8820907	0.0352159	3.0393014
C	54	40	39	3.2304710	101.8092349	152.9038591	-4.4320358	3.8286662	0.0572012
C	74	54	40	1.5462959	82.9014152	135.5412655	-4.0114372	4.0407691	-1.4155989
C	58	2	1	3.5932401	144.0255504	-113.3840633	-0.1932375	4.1323952	-0.4933988
C	76	58	2	1.5425114	91.8928219	-85.6196321	0.1832590	4.6495978	-1.8969989
H	74	54	40	1.1188025	39.6008017	-91.7141496	-5.0641295	2.9089619	0.1367012
H	75	74	54	1.1160679	110.7324421	-152.1546080	-3.4081435	4.9734733	-1.5237989
H	76	58	2	1.1187073	51.5641404	29.6267229	-1.0365326	3.3997894	-0.5537988
H	77	76	58	1.1109513	109.3219671	-45.4824659	1.0208632	4.0414035	-2.3003990
H	74	54	40	1.1099587	144.4765201	-111.6118890	-5.0764416	4.6753619	0.3732012
H	75	74	54	1.1088442	110.3894530	88.1823146	-4.9065379	4.1325630	-2.0635989
H	76	58	2	1.1226818	67.9871965	163.7845348	0.6713664	3.5686010	-0.0517988
H	77	76	58	1.1142260	109.9022717	-161.2720388	0.5703519	5.6920005	-1.8258989
N	77	76	58	1.4957959	110.1406602	79.0016285	-1.0186411	4.6441896	-2.7873990
H	86	77	76	1.0239108	109.9107137	151.5226424	-0.9286461	5.3747902	-3.4990990
N	76	58	2	1.4944537	157.3040329	83.0028762	-0.4746454	5.2779933	0.4241012
H	88	76	58	1.0276140	109.1055956	-125.2261607	-1.0355502	5.9791896	-0.0755988
N	75	74	54	1.5183519	108.7036335	-32.6758355	-3.1674290	2.8579748	-1.8560989
H	90	75	74	1.0644203	107.0391992	-61.3613922	-2.3051289	2.8405807	-1.2322989

N	74	54	40	1.4863795	91.9155099	27.7736464	-3.1955345	3.6622747	0.8651013
H	92	74	54	1.0366491	110.6797571	-54.1865680	-3.3082293	2.8950738	1.5531013
C	90	75	74	1.5157420	113.2300066	177.9363049	-2.7387296	2.9370777	-3.3077990
H	94	90	75	1.1077987	110.7086461	-19.3281356	-3.3848344	3.6402734	-3.8692991
H	94	90	75	1.1286150	107.9422199	-137.1590599	-2.8645226	1.9123768	-3.7637991
C	86	77	76	1.4916056	112.9168493	-85.1509706	-1.2539321	3.3224879	-3.4374990
H	97	86	77	1.1207668	111.8620458	12.4173471	-0.6290265	2.5138921	-2.9772990
H	97	86	77	1.1115141	112.9458924	-105.7415418	-0.9835320	3.3155897	-4.5155991
C	92	74	54	1.4912652	114.4408413	-179.3046468	-2.7355430	4.9034779	1.5519013
H	100	92	74	1.1099988	110.7102017	-27.9717257	-3.0542491	5.8050758	0.9883013
H	100	92	74	1.1119878	112.0823844	90.3186970	-3.1725437	5.0046749	2.5694014
C	88	76	58	1.4899860	112.9877005	-3.5831210	-1.1938426	4.8681884	1.6630013
H	103	88	76	1.1141202	106.1522123	149.6689334	-0.8699474	5.5777907	2.4585014
H	103	88	76	1.1183773	110.9421436	35.3874822	-0.8572357	3.8579906	2.0050014
H	58	2	1	2.6404843	138.7744251	100.6839732	2.3952803	1.5506127	-1.5193989
C	76	58	2	3.6373076	79.4238472	178.5729803	3.1816691	3.1967182	0.4887012
C	107	76	58	1.5439929	106.8972726	60.5915105	3.9297719	2.7965232	-0.8012988
C	57	18	17	3.2990364	153.9992624	77.7060895	6.2460887	0.3587389	0.7792013
C	109	57	18	1.5416205	107.9190323	35.3758999	7.1373886	0.3836449	-0.4783988
H	107	76	58	1.1232331	16.6144151	-45.2831235	2.0712690	3.1980106	0.3194012
H	108	107	76	1.1237285	109.7261063	169.9703665	5.0251728	2.6746307	-0.5821988
H	109	57	18	1.1200458	18.4119379	138.6712261	5.1609889	0.3154315	0.5050012
H	110	109	57	1.1113300	109.0877474	-75.9547414	7.4648957	-0.6522529	-0.7122988
H	107	76	58	1.1129899	91.7158186	170.2915378	3.4402619	4.2522200	0.7291013
H	108	107	76	1.1069317	110.8916121	51.8454815	3.8376665	3.5857227	-1.5719989
H	109	57	18	1.1127460	90.5599575	-75.3780845	6.4476950	-0.5690598	1.3595013
H	110	109	57	1.1143154	109.9264326	168.1470324	8.0674847	0.9620513	-0.2732988
N	110	109	57	1.4981653	111.1505773	48.7803953	6.4328841	1.0378402	-1.6273989
H	119	110	109	1.0246643	109.3792112	163.5854624	7.1171824	1.2879449	-2.3478990
N	109	57	18	1.4973677	129.2017040	171.6122988	6.5857808	1.5184413	1.6634013
H	121	109	57	1.0266741	108.8818720	-86.2459874	6.5986750	2.3750414	1.0976013
N	108	107	76	1.5126819	110.3858270	-71.2621846	3.4105809	1.4750196	-1.3230989
N	107	76	58	1.4830750	125.8076115	-68.3527398	3.5384757	2.2334205	1.5584013
H	124	107	76	1.0411475	110.5208473	-4.3526211	2.6835779	1.9043147	2.0532014
C	123	108	107	1.5190961	113.1133832	-178.4444989	4.1318841	1.0029245	-2.5738990
H	126	123	108	1.1070409	110.7507199	-35.9207226	4.3966783	1.8609263	-3.2213990
H	126	123	108	1.1261191	107.6945579	-154.4977309	3.4293887	0.3294196	-3.1404990
C	119	110	109	1.4913699	112.4417805	-74.1965700	5.3751899	0.1672329	-2.2168990
H	129	119	110	1.1243266	110.8969024	19.5530541	5.0684954	-0.6369692	-1.4934989
H	129	119	110	1.1106489	113.0965398	-98.5589186	5.7113936	-0.3699648	-3.1289990
C	124	107	76	1.4912871	114.2917918	-128.8559749	4.5269722	2.7527273	2.5469014
H	132	124	107	1.1096218	111.8958480	-12.1182293	4.9983658	3.6968306	2.2038014
H	132	124	107	1.1131352	111.1036528	106.1690267	4.0364706	2.9894240	3.5177015
C	121	109	57	1.4912223	112.4621796	35.0770238	5.6170796	1.6825347	2.7852014
H	135	121	109	1.1139645	106.0624668	141.3699128	6.2210776	1.9784388	3.6732015
H	135	121	109	1.1159850	110.8355249	26.5154977	5.1402862	0.7072313	3.0438014

Interaction Energies

$[Gd(DOTP)]^{5-}$/Cyclen (1:2)
CP-corrected interaction energy: 282 kcal/mol

The interaction energies for the 1:1 adducts which we call A and B were found as follow:
From the optimized $[Gd(DOTP)]^{5-}$/Cyclen (1:2) complex, one of the cyclen unit was removed and the interaction energy computed, after that the procedure was repeated removing the other cyclen unit.

$[Gd(DOTP)]^{5-}$/Cyclen (1:1) A
CP-corrected interaction energy: 104 kcal/mol

$[Gd(DOTP)]^{5-}$/Cyclen (1:1) B
CP-corrected interaction energy: 98 kcal/mol

R_1 dependence for $[Gd(DOTP)]^{5-}$ (1.0 mM) in increasing concentration of the substrates (Titration data)

Gd(III)-complex (**1**) with polyamine **2** (32 MHz, 298 K)

[cyclen] / M	**R_1 / s^{-1}**
0	5.0
0.0015	5.3
0.0029	5.7
0.0058	6.3
0.0075	6.8
0.011	7.0
0.012	7.4
0.01451	7.8
0.018	7.9
0.023	8.2
0.02902	8.6
0.035	8.7
0.04	8.9
0.05224	9.1
0.067	9.1
0.08	9.3
0.095	9.4
0.11029	9.5

Gd(III)-complex (**1**) with polyamine **3** (32 MHz, 298 K)

[octaazacryptand] / M	R_1 / s^{-1}
0	5.0
0.0008	6.3
0.00135	7.5
0.0019	9.0
0.0027	10.1
0.0035	11.2
0.00472	12.1
0.00623	12.5
0.00742	13.5
0.0085	15.0
0.01079	15.9
0.012	17.0
0.01484	17.8
0.01889	19.2
0.022	19.5
0.02564	20.9
0.029	20.8
0.035	22.0
0.03913	22.0
0.045	22.2
0.05262	23.2
0.062	23.2
0.07286	23.6
0.09984	24.0

Gd(III)-complex (**1**) with polyamine **4** (32 MHz, 298 K)

[PEI] / M	R_1 / s^{-1}
0	5.0
0.000012	6.0
0.000021	7.5
0.000027	8.3
0.000033	9.3
0.000042	10.5
0.000054	12.0
0.00006	13.0
0.00007	14.0
0.000081	15.5
0.00009	16.4
0.000108	18.5
0.00012	20.0
0.000135	21.4
0.00015	22.0
0.000162	23.0
0.000189	24.0
0.000216	25.0
0.000243	25.5
0.00027	26.0
0.00033	26.4
0.00038	26.5
0.00043	26.5
0.00048	27.0
0.000545	27.0
0.0006	27.0
0.000655	27.2

^{1}H NMRD profiles for $[Gd(DOTP)]^{5-}$, the adducts with cyclen (2), octaazacryptand (3) and PEI (4) and NG/$[Gd(DOTP)]^{5-}$ at 298 K.

	$[Gd(DOTP)]^{5-}$	- 2	- 3	-4	NG/$[Gd(DOTP)]^{5-}$
Proton Larmor Frequency / MHz	r_1 / mM^{-1} s^{-1}	r_1 / mM^{-1} s^{-1}	r_1 / mM^{-1} s^{-1}	r_1 / mM^{-1} s^{-1}	r_1 / mM^{-1} s^{-1}
0.00997	7.2	14.5	25.1	28.1	39.8
0.01436	7.3	14.6	24.7	28.5	40.0
0.0207	7.3	14.5	25.0	28.2	39.1
0.02973	7.3	14.5	25.2	28.5	40.1
0.04287	7.2	14.4	24.9	28.9	39.6
0.06162	7.3	14.3	24.6	28.7	39.9
0.08854	7.3	14.4	24.9	28.7	39.8
0.12749	7.4	14.5	24.4	28.4	39.5
0.18317	7.3	14.4	24.4	28.3	39.2
0.26376	7.3	14.3	24.2	27.9	39.1
0.37932	7.4	14.1	23.9	27.3	38.2
0.54549	7.2	14.0	22.9	26.9	37.2
0.7845	7.2	13.7	22.1	25.9	36.0
1.1292	7.2	13.4	21.1	24.5	34.2
1.6235	7.1	13.2	20.5	23.6	32.4
2.3363	7.0	12.6	19.4	22.0	31.8
3.3598	6.9	12.1	19.0	21.5	30.7
4.8321	6.5	11.1	17.8	20.5	28.7
6.9526	5.9	10.2	18.1	20.2	28.1
9.9994	5.3	9.5	19.1	20.9	30.0
22	4.6	9.5	24.4	26.4	43.3
32	4.3	9.4	25.0	27.0	42.5
42	4.3	9.3	23.9	26.2	39.8
52	4.3	9.3	21.7	24.8	36.4
62	4.3	9.3	19.3	23.7	33.3
82	4.3	9.2	17.3	21.3	29.4
120	4.4	9.1	14.0	17.5	26.4

References

1. D. H. Powell, O. M. N. Dhubhghaill, D. Pubanz, L. Helm, Y. S. Lebedev, W. Schlaepfer, A. E. Merbach, *J. Am. Chem. Soc.*, 1996, **118**, 9333-9346.
2. F. Kielar, L. Tei, E. Terreno, M. Botta, *J. Am. Chem. Soc.*, 2010, **132**, 7836-7837.
3. F. Uggeri, S. Aime, P. L. Anelli, M. Botta, M. Brocchetta, C. de Haën, G. Ermondi, M. Grandi, P. Paoli, *Inorg. Chem.,* 1995, **34**, 633–643.
4. S. Aime, M. Botta, E. Terreno, P. L. Anelli, F. Uggeri, *Magn. Reson. Med.*, 1993, **30**, 583-591.
5. S. Aime, M. Botta, M. Fasano, S. G. Crich, E. Terreno, *J. Biol. Inorg. Chem.*, 1996, **1**, 312-319.
6. R. N. Muller, B. Radüchel, S. Laurent, J. Platzek, C. Piérart, P. Mareski, L. Vander Elst, *Eur. J. Inorg. Chem.*, 1999, 1949-1955.